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R603

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(58) Field of search

UK CL (Edition K) C7F FHB FHE FHZ, D1P PDZ,

D1R RFA RFZ

INT CL⁵ C23C, D04H, D06M

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(54) Boron nitride coated fibres

(57) Thick BN (boron nitride) coatings having a thickness of at least 0.4 microns protect fibres, increase their fracture toughness, and decrease chemical interaction between the fibres and the matrix into which they are to be incorporated. The boron nitride coating may be produced from the reactant gases boron trichloride and ammonia at a temperature of 1000-1300°C using argon as a carrier gas. The fibre may consist of mullite, silicon nitride or an alumina base, and the coated fibre may be encased in a matrix selected from glass, glass-ceramic, ceramic including chemical vapour infiltrated silicon carbide and silicon carbide, thermoset material, thermoplastic material, and metal to form a composite material. The fibres may be set in an array in the matrix and the composite exhibits fibre pullout during fracture.

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FIG.1

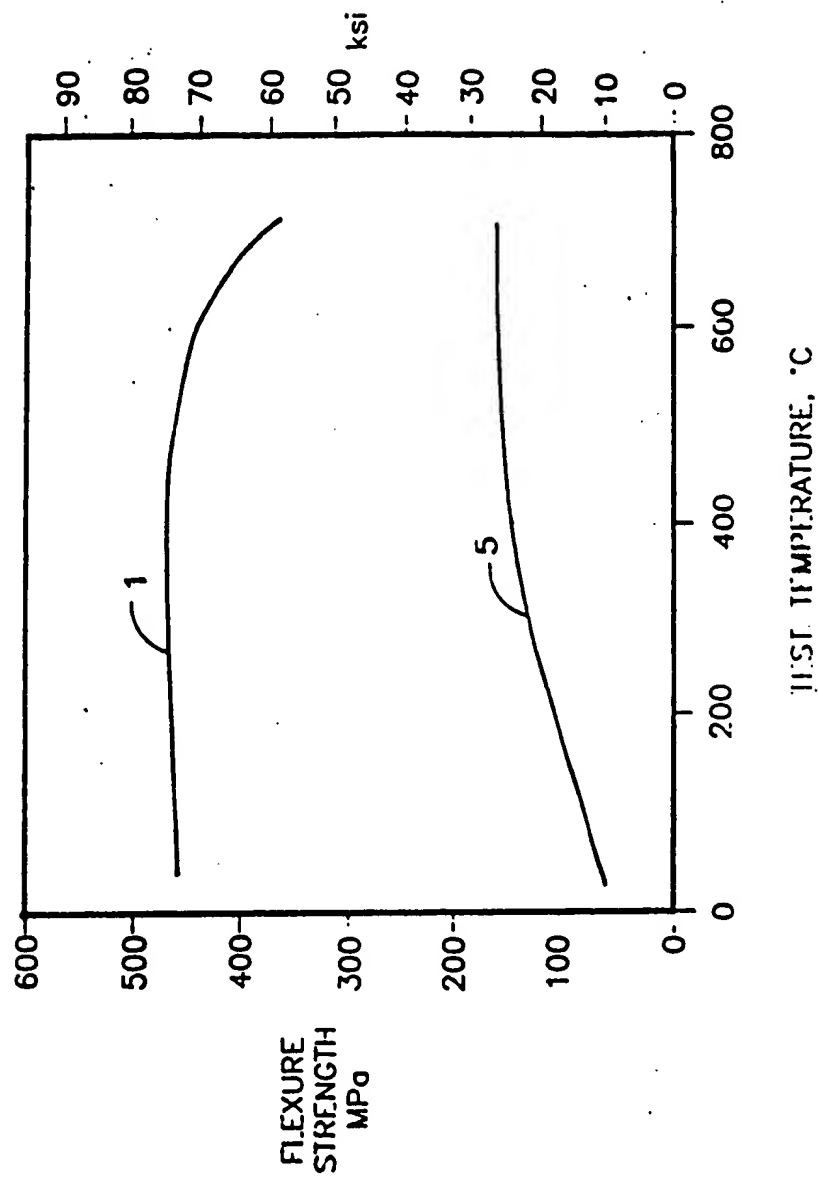


FIG. 2A

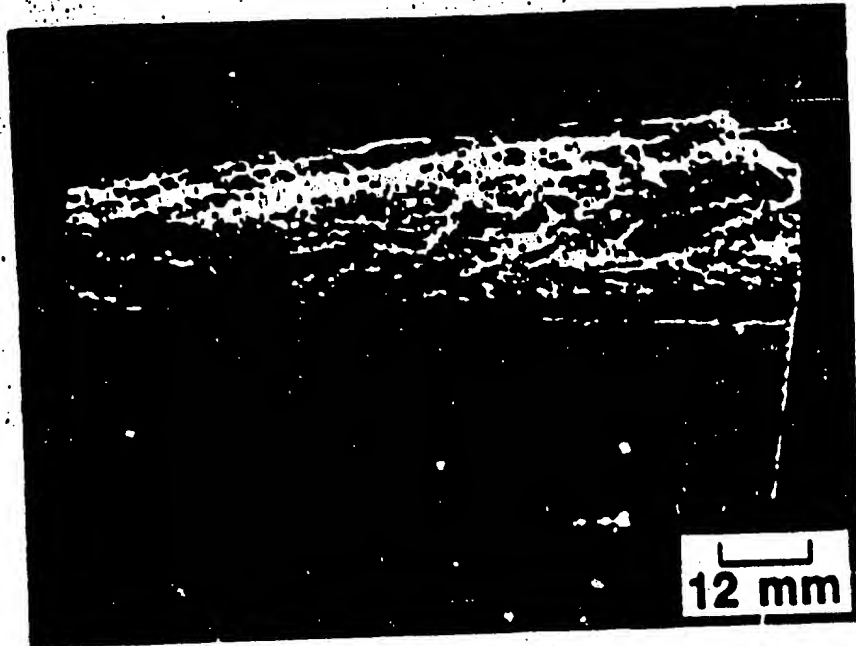


FIG. 2B

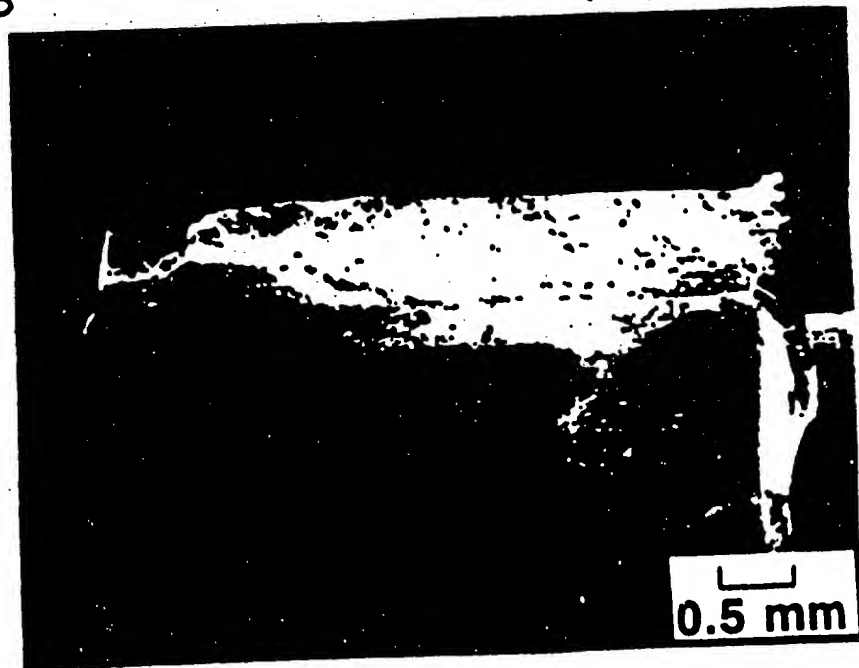


FIG. 2C

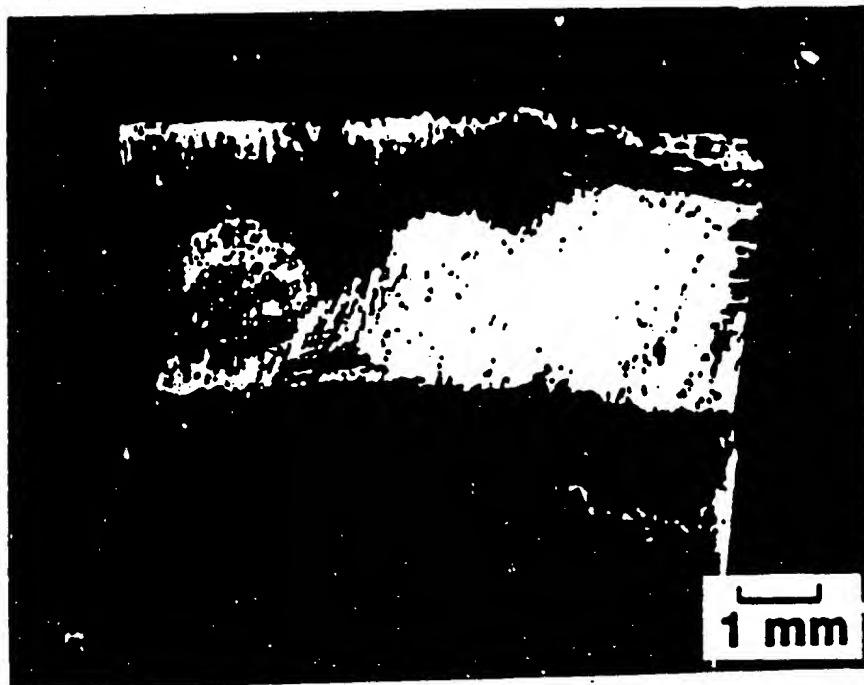
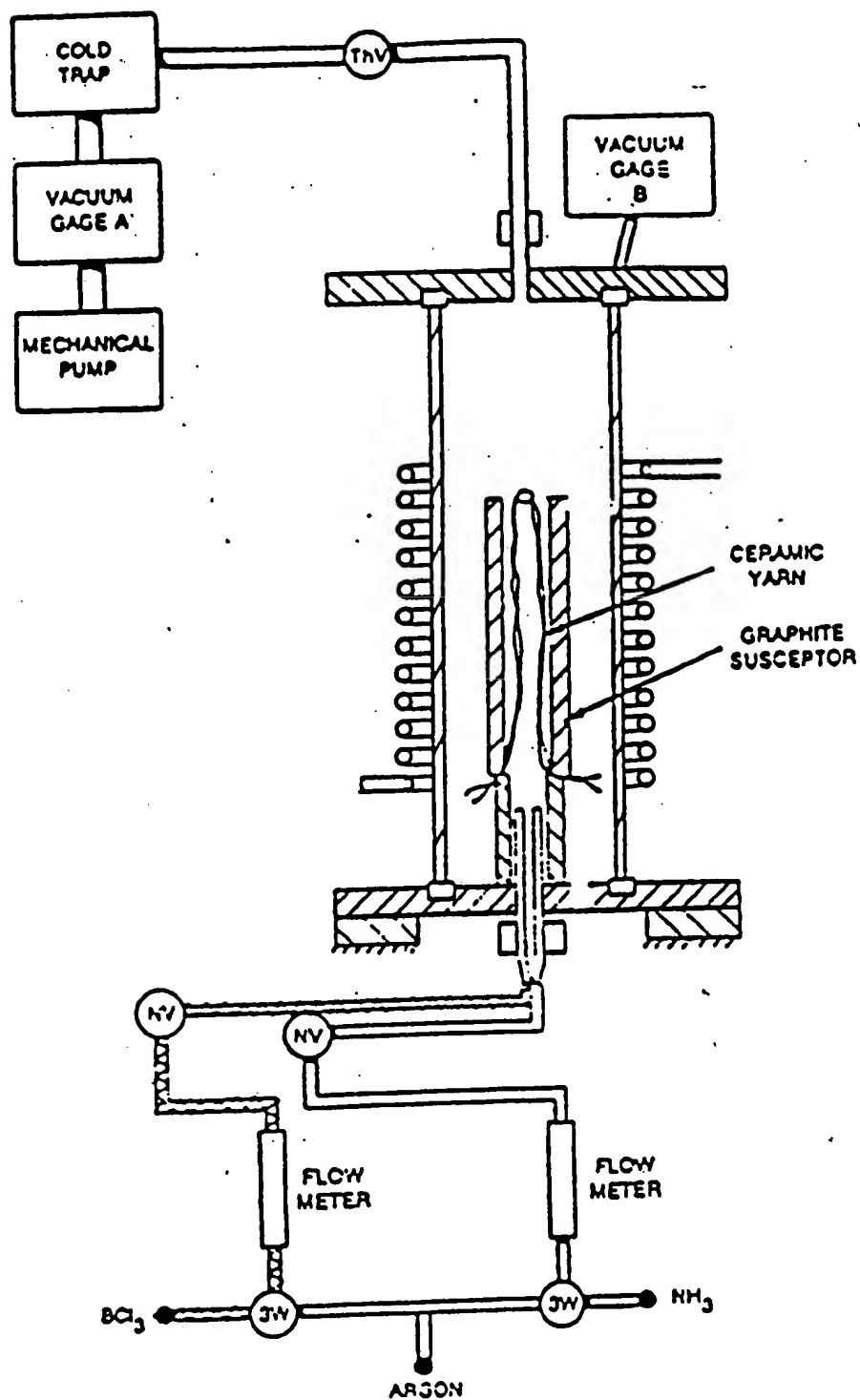


FIG. 3



- (JW) = 3 WAY VALVE
- (NV) = NEEDLE VALVE
- (TV) = THROTTLE VALVE
- ~~~~~ = HEATED

Description

BN Fiber Coatings

Technical Field

This invention relates to coating fibers, and specifically to coating fibers with a thick layer of BN, and to the resultant coated fibers.

Background Art

Fiber reinforcement of glass, glass-ceramic, ceramic, metal, thermoset, and thermoplastic materials, can increase their strength; broadening the spectrum of possible applications. However, strong matrix/fiber bonding, especially in ceramic composites, can cause brittle fracture which results in substantially flat fracture surfaces with virtually no fiber pull out, decreasing fracture toughness. Fiber pullout increases the distance traveled by failure cracks, increasing their surface area and the toughness of the composite.

The application of a coating, for example carbon, to the fibers prior to matrix formation can reduce matrix/fiber bonding and chemical interaction; improving fracture toughness. Carbon coatings (see for example U.S. Pat. Nos. 4,425,407 and 4,731,298; incorporated herein by reference), which are easily oxidized and highly electrically conductive, have limited use under certain conditions.

Boron nitride (BN), possessing high electrical resistance, excellent thermal-shock resistance, and noncombustibility, is similarly used as a fiber coating. (See U.S. Pat. No. 4,642,271 incorporated

herein by reference.) Due to its graphite-like hexagonal plate structure, BN is similar to carbon without some of carbon's limitations; a viable substitute.

5 BN coatings can be applied using CVD (chemical vapor deposition) at temperatures ranging from about 850°C to about 2200°C. However, stoichiometric BN coatings have only been achieved at deposition
10 temperatures greater than 1700°C; a temperature which usually causes significant fiber degradation. When fibers are heated to such temperatures, cooled, and tested at room temperature, they fail to retain their original strength. Furthermore, the BN coatings
15 achieved utilizing the prior art are thin, generally less than about 0.35 microns, with thick coatings only achieved at temperatures above 1400°F (U.S. Pat. No. 4,481,257 incorporated herein by reference). As a result, the search continues for improved fiber coatings and application methods.

20 Disclosure of Invention

This invention involves coating fibers with BN to increase fracture toughness and decrease chemical
25 reaction between the fibers and the matrix. Fibers are placed within a CVD reactor and heated. Reactant gases, containing both boron and nitrogen are introduced into the reactor via a carrier gas. The
30 gases react to produce BN, deposition occurs, and a thick BN coating is formed around the fibers (ie., greater than about 0.40 microns); a thickness necessary to obtain the desired toughness and reduce chemical reaction between the fibers and the matrix.

The foregoing and other features and advantages of the present invention will become more apparent from the following description and accompanying drawings.

5 **Brief Description of Drawings**

Fig. 1 shows a graph of the flexure strength versus temperature of coated and uncoated fibers within a composite.

Fig. 2 shows a comparison of fracture surfaces for various BN coating thickness.

Fig. 3 shows the CVD reactor assembly used in the application of the BN coating.

Best Mode for Carrying Out the Invention

15 Brittle fracture is a significant problem in ceramic composites composed of uncoated or thinly coated fibers embedded within a ceramic matrix. The brittleness of the composites causes cracks, resulting from fractures due to stress, to run virtually straight through the composite. However, if the fibers within the matrix are sufficiently coated with
20 BN, the BN coating increases fracture toughness thru crack deflection and blunting, preventing brittle fracture. Applying stress to the composite with BN coated fibers results in fiber pullout, as opposed to a smooth fracture surface. Yet, not all BN coatings
25 achieve fiber pullout; if the BN coating thickness is around or below about 0.30 microns, a smooth fracture surface results, similar to composites containing uncoated fibers.

Fig. 1 shows the flexure strength results of
30 coated and uncoated fiber composites of Nextel™

fibers embedded in a glass matrix. The composite with the BN coated fibers (according to the invention) (1) has a flexure strength significantly greater than that of the composite with the uncoated fibers (5).

5 Figures (2A), (2B), and (2C) shows a comparison of fracture surfaces for BN coating thickness of 0.08 microns (Fig. 2A) and 0.16 microns (Fig. 2B) (as claimed in U.S. Pat. No. 4,642,271). Both surfaces reveal fairly smooth fracture surfaces. Figure (2C),
10 on the other hand, shows substantial fiber pullout for fibers with a BN coating thickness of 1.14 microns.

Various fibers, such as silicon nitride, mullite, and alumina based fibers can be used in this process, with Nextel 480 produced by 3M Co., MN and Sumitomo[™]
15 Al_2O_3 preferred. Matrices, such as glass, glass-ceramic, ceramics (including CVI silicon carbide and silicon nitride), thermoplastic material, thermosets, and metal can be used to enclose the above mentioned fibers.

20 Furthermore, various reactant gases containing boron and nitrogen may also be used; BCl_3 (boron trichloride) and NH_3 (ammonia) have proven particularly suitable. These reactant gases are introduced to the reactor via a carrier gas.

25 Hydrogen (H_2), a commonly used carrier gas, has proven unsuitable for this process. H_2 causes degradation and weakening of fibers. An inert gas, such as argon (Ar), usually degrades fibers less than the common standard gas, H_2 . As a result, an inert
30 gas, Ar in particular, was used as the carrier gas for this invention.

The following table shows the results of coated Nextel 480 fibers held at the given temperature for 3 minutes with H₂ or Ar as the carrier gas.

5	Purge	Temp. °C	RT Tensile
	Gas		Strength (ksi)
	H ₂	1050	155
	H ₂	1080	122
	H ₂	1100	too weak to test
	Ar	1050	378
10	Ar	1060	251
	Ar	1100	129
	Ar	1150	98
	Ar	1200	84

15 This invention will be clarified by references to the following illustrative examples.

EXAMPLE 1

The following procedure is used to form a BN coating on Nextel 480 fibers.

- 20 1. A graphite susceptor, 2.0 inches in diameter (1/8 inch wall thickness) and 4.0 inches long which has Nextel fibers arranged within it, is loaded into a CVD reactor, 3.0 inch in diameter by 16.0 inch in length (See Fig. 3).
- 25 2. The reactor is pressurized to 200 microns and heated to 1050°C.
3. The reactant and carrier gases are flowed thru the system: BCl₃ at 67 cc/min, NH₃ at 67 cc/min, and Ar at approximately 208 cc/min, for 3

minutes; producing a BN coating approximately 1.30 microns thick.

EXAMPLE 2

5 The parameters given in Example 1 are followed, substituting Sumitomo for the Nextel 480, a coating thickness of approximately 0.80 microns can be obtained.

10 The coating thickness given in Examples 1 and 2 can be increased by changing the concentration of the BCl_3 and NH_3 (decrease the amount of carrier gas; Ar), or by increasing the run time.

15 Although this invention has been shown and described with respect to detailed embodiments thereof, it will be understood by those skilled in the art that various changes in form and detail thereof may be made without departing from the spirit and scope of the claimed invention.

We claim:

Claims

1. A boron nitride (BN) coating, said coating having a thickness of at least 0.40 microns, surrounding fibers to be embedded within a matrix, whereby the coating is sufficient to inhibit both physical bonding and chemical interaction between the matrix and the fibers, wherein fracture toughness is increased through crack deflection and blunting, causing fiber pullout to occur when stress is applied to the fiber/matrix system.
2. A method of producing a boron nitride (BN) coating on fibers to be embedded within a ceramic matrix, using a carrier gas, being produced from reactant gases, which comprises:
 - a. using reactant gases, said gases containing boron and nitrogen;
 - b. using an inert gas as the carrier gas;
 - c. applying the coating at a temperature between about 1000°C and 1300°C;whereby the temperature is determined by a balance between the desired purity of the BN coating and the possible fiber degradation.
3. A method as in claim 2 using argon as the inert carrier gas.
4. A method as in claim 2 using boron trichloride (BCl_3) and ammonia (NH_3) as the reactant gases.

5. A fiber selected from the group consisting of mullite, silicon nitride, and alumina base fibers, having on its surface a coating of BN at least about 0.40 microns thick, said coated fiber being encased in
5 a matrix selected from the group consisting of glass, glass-ceramic, ceramic (including CVI silicon carbide and silicon nitride), thermoset, thermoplastic material, and metal.
6. A composite material consisting of a BN coated
10 fibers, said fibers in an array, and a matrix, said composite exhibiting fiber pullout during fracture.
7. A composite material as in claim 6 wherein the BN coating thickness is at least about 0.40 microns.

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